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Hagting, J.G.; Schouten, A.J.; Hagting, A

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Oxidation of Monolayers of Partly Converted Dimethoxy-Substituted Poly(*p*-phenylenevinylene) Precursor Polymers at the Air–Water Interface

J. G. Hagting and A. J. Schouten*

Department of Polymer Science, University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands

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We observed that the poly(*p*-phenylenevinylene) units in Langmuir monolayers of partly converted dimethoxy-substituted poly(*p*-phenylenevinylene) precursor polymers oxidize at the air–water interface. This reaction even happened in the dark and therefore can not be attributed to a photooxygenation reaction with singlet oxygen. We assume that ground-state triplet oxygen is polarized at the air–water interface and forms a weakly bound complex with the double bond to give a reactive intermediate state, which lowers the activation energy of the oxidation reaction. The air–water interface thus works as a catalyst in this reaction.

Introduction

In previous articles the behavior and structure of monolayers of different (di)alkoxy-substituted poly(*p*-phenylenevinylene) (PPV) precursors were studied by surface pressure–area isotherms, Fourier transform infrared (FT-IR) reflection measurements at the air–water interface, and hysteresis experiments.^{1,2} The precursor polymers formed true 2D stable monolayers at the air–water interface in which all polymer segments are in contact with the water subphase. Immediately after spreading, the aromatic rings of dimethoxy-substituted precursor (prec-DMePPV) take on a more-or-less perpendicular orientation to the surface, and the monolayer is about 8 Å thick. The transfer of prec-DMePPV was only successful for the first monolayer. The transfer improved when the precursor was partially converted to PPV.^{3,4} During stabilization experiments of these partly converted precursor monolayers, we discovered that the monolayer oxidizes at the air–water interface.

Oxidation reactions of conjugated polymers have been described well^{5,6} and greatly impede the application of conjugated polymers in devices such as light-emitting diodes (LEDs) and photovoltaic cells, because the formed carbonyl groups are exciton quenchers.⁷ These oxidation reactions are photooxygenation reactions, wherein the conjugated polymer itself acts as the photosensitizer for singlet oxygen.^{8,9}

The oxidation reaction of the partly converted precursor PPV monolayers described in this article is not a photo-

oxygenation reaction, because it also happens in the dark. We synthesized several partly converted dimethoxy-substituted precursor PPVs with different percentages of conjugated units and studied the oxidation reaction thoroughly under various conditions.

Experimental Details

Materials. The preparation of precursor polymer poly[2,5-di-methoxy-1,4-(α -methoxy)xylylene] (prec-DMePPV) (see Scheme 1) was described previously.¹

Partly converted DMePPVs were prepared by dissolving 300 mg (1.5 mmol) prec-DMePPV in 30 mL 1,2,4-trichlorobenzene. This solution was degassed and allowed to reflux under an inert nitrogen atmosphere. After 5, 10, and 15 min of reflux a part of the solution was precipitated in cold methanol. The partly converted precursors obtained were redissolved in dichloromethane and were precipitated again in cold methanol.

¹H NMR. ¹H NMR spectra were recorded in chloroform-*d*₁ solutions at 200 MHz.

IR. The oxidized monolayers were collected by moving the moveable barrier toward the fixed barrier until the distance between the barriers was equal to the width of a small silicon wafer, and the monolayer subsequently was swept together and picked up by the silicon wafer. After that the collected monolayer was dried and analyzed using in a Mattson Galaxy 6021 FT-IR spectrometer.

UV–Visible. The UV–Vis spectra of the oxidized monolayers were taken by dissolving the collected material on the silicon wafer in chloroform (Uvasol quality) after the IR spectrum was taken. The spectra were recorded on a SLM Aminco 3000 diode-array UV–Vis spectrophotometer.

Langmuir Films. The surface pressure isotherms and the stabilization experiments were performed on a computer-controlled Lauda Filmbalance (FW 2). The surface pressure could be measured with an accuracy of 0.05 mN/m. The partly converted precursors were spread from chloroform solutions (Uvasol quality, concentrations 0.2–0.4 mg/mL) onto pure water subphase, which was purified by reverse osmosis and subsequent filtration through a Milli-Q purification system or onto a water subphase to which HCl, KHCO₃, 3×10^{-3} M ascorbic acid or 1×10^{-3} M 3-carboxypropyl had been added. The solutions were stored in the dark, and a drop of pyridine was added to prevent premature elimination by acidic products in chloroform.^{3,10}

Ozone Test. The presence of ozone in the laboratory air was tested with Dräger Röhrchen testing tubes with a measurable range of 0.05–1.4 ppm.

Gel Permeation Chromatography. Gel permeation chromatography (GPC) measurements were performed on chloroform

* E-mail: A.J.Schouten@chem.rug.nl.

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Scheme 1

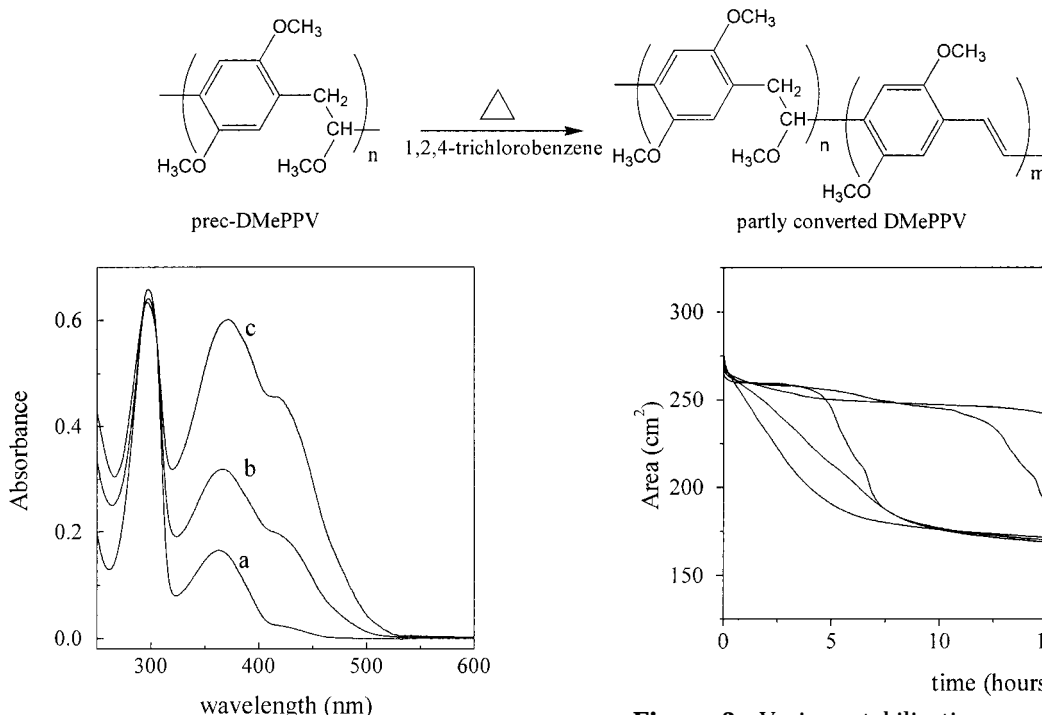


Figure 1. UV-Vis spectra of partly converted prec-DMePPVs dissolved in chloroform. (a) 10% conversion, (b) 20% conversion, and (c) 32% conversion. Concentration = 0.023 mg/mL.

solutions in a Spectra Physics AS 1000 system using universal calibration with a Viscotek H-502 viscometer and a Shodex RI-71 refractive index detector. CHCl_3 was used as eluent. The columns were calibrated with polystyrene standards.

Results and Discussion

The UV-Vis spectra of the partly converted precursors dissolved in chloroform are shown in Figure 1.

The strong band at $\lambda = 290$ nm, corresponds to the $\pi-\pi^*$ transition of the dimethoxy-substituted phenyl ring. The bands with λ_{max} at 360 nm and λ_{max} at 410 nm correspond to conjugated units, the tetramethoxystilbene unit and the hexamethoxydistyrylbenzene units, respectively.¹¹ Using ^1H NMR spectroscopy, the degree of conversion was calculated on the basis of the peaks between 3.5 and 4 ppm originating from the methyl protons of the aromatic methoxy groups of the PPV and the precursor-PPV units and the bands between 2.7 and 3.3 ppm which originate only from groups of the precursor-PPV unit. The conversion of the polymer was determined to be 10%, 20%, and 32% after 5, 10 and 15 min of reflux, respectively.

Various stabilization curves of the 32% partly converted prec-DMePPV (32%-pcDMePPV) at 15 mN/m and 15 °C are shown in Figure 2.

This experiment is qualitatively reproducible but not quantitatively reproducible. All experiments showed the same large decrease in area, but the moment at which the decrease started and the rate differed from experiment to experiment. After the initial decrease in area a more-or-less stable monolayer was formed. The stabilization curves of 10%-pcDMePPV, 20%-pcDMePPV, and 32%-pcDMePPV at a surface pressure of 15 mN/m and at 15 °C are shown in Figure 3. The results show that the total decrease in area depends on the degree of conversion of the polymer.

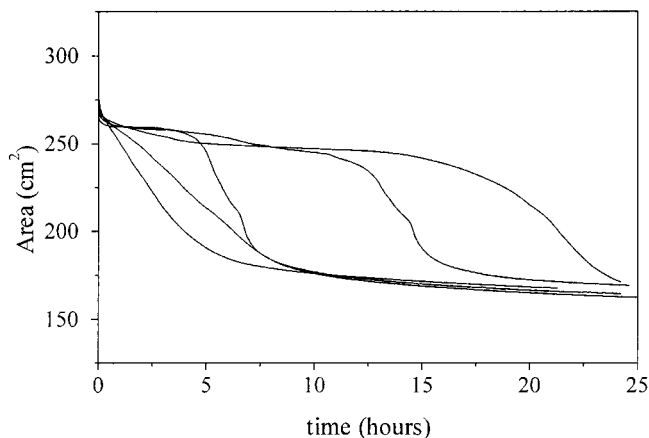


Figure 2. Various stabilization curves of 32%-pcDMePPV stabilized at 15 mN/m and 15 °C.

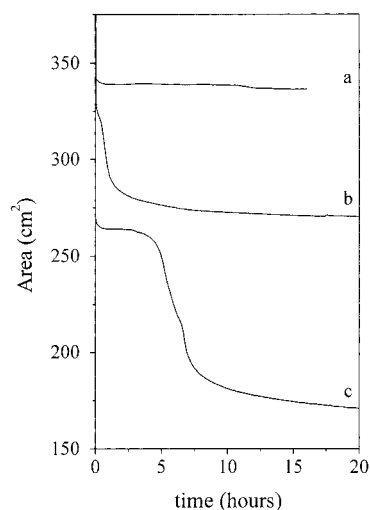


Figure 3. Stabilization curves of (a) 10%-pcDMePPV, (b) 20%-pcDMePPV, (c) 32%-pcDMePPV stabilized at 15 mN/m and 15 °C.

The 32%-pcDMePPV monolayer was collected after the decrease in area and UV-Vis and FT-IR spectra were taken with this material (for procedure see Experimental Details). The UV-Vis spectra of 32%-pcDMePPV and of the collected monolayer, both being dissolved in chloroform, are shown in Figure 4.

The absorption bands of the longer conjugated units have disappeared in the UV-Vis spectrum of the collected monolayer and only the absorption of the stilbene units can be observed. A band with λ_{max} at 266 nm has appeared, which can be attributed to the $n-\pi^*$ transition of a carbonyl group.¹² In Figure 5 the FT-IR spectrum of 32%-pcDMePPV before spreading (Figure 5a) and the FT-IR spectrum of the collected monolayer (Figure 5b) are shown.

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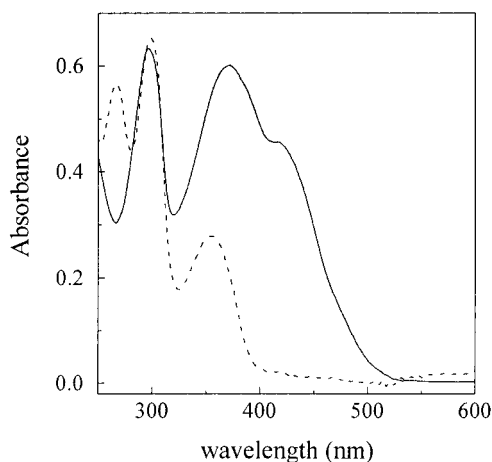


Figure 4. UV-Vis spectra 32%pc-DMePPV (solid line) and of the monolayer collected after the decrease in area (dashed line), both dissolved in chloroform. Concentration = 0.023 mg/mL.

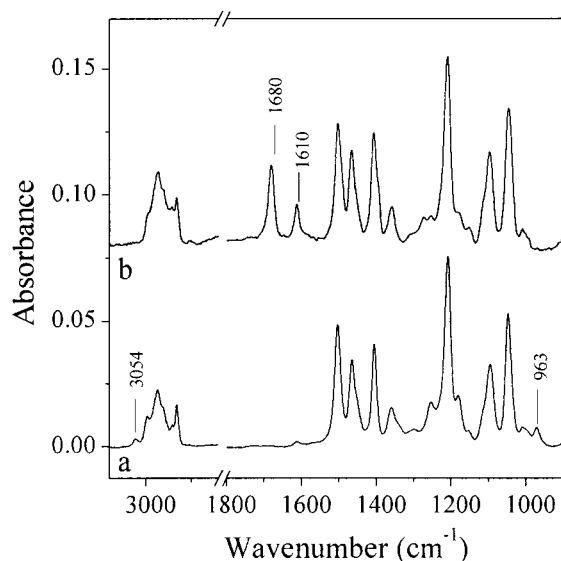


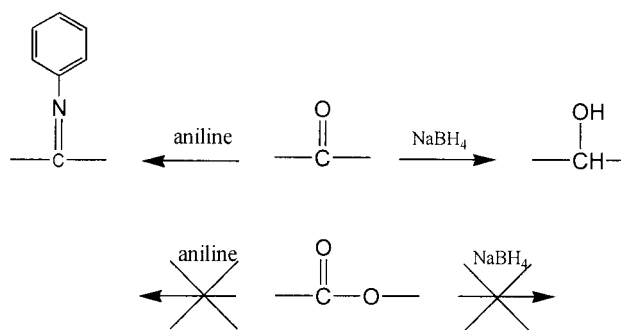
Figure 5. FT-IR spectra of (a) 32%pc-DMePPV film on silicon wafer, and (b) collected monolayer of 32%pc-DMePPV after the decrease in area on silicon wafer.

When the spectra of Figure 5 are compared, the appearance of a peak at 1680 and 1610 cm^{-1} is observed and a decrease in the vinyl bands at 3054 and 963 cm^{-1} . The band at 1680 cm^{-1} can be attributed to carbonyl groups, whereas the band at 1610 cm^{-1} originates from nonsymmetrically substituted aromatic ring vibration.⁶ When the reducing agent NaBH_4 or aniline is added to a solution of the collected monolayer the band at 1680 cm^{-1} diminishes, meaning that it can be attributed to an aldehyde or ketone group and not to an ester group (Scheme 2).¹³

Whereas the weight-average molecular weight (\bar{M}_w) of the 32%-pcDMePPV before spreading is about $1 \cdot 10^6$, the \bar{M}_w of the collected material, after oxidation, as determined by GPC, is about $4 \cdot 10^3$. Therefore, it is very likely that double bonds in the partly converted monolayers at the air–water interface are oxidized to aldehyde groups, thus decreasing the average molecular weight.

When no pressure was applied to the monolayer after spreading and the remaining polymer at the air–water interface was collected after 24 h and analyzed, it appeared

Scheme 2



that the oxidation reaction had occurred, which means that an applied surface pressure is not needed for this reaction.

We assume that the observed decrease in the monolayer area does not correspond with the initiation of oxidation, but with the moment that low molecular weight products with carbonyl ends, that are formed by oxidation, begin to dissolve in the subphase.

The oxidation reaction could be prevented when oxygen in the subphase was thoroughly removed ultrasonically and by placing the Langmuir–Blodgett (LB) trough under an argon atmosphere.

The oxidation of double bonds to aldehyde groups is a very well-known photooxygenation reaction.¹⁴ This reaction involves singlet oxygen that is produced by energy transfer from triplet sensitizers to oxygen. To reach the triplet state the sensitizer needs to absorb light. The PPV units in the partly converted precursor can act as sensitizers.^{8,9}

Oxidation with triplet oxygen is spin forbidden but is rarely observed in electron-rich conjugated systems.^{15,16}

In our case the oxidation reaction also happened when the monolayer was spread in complete darkness. However, the bulk material did not oxidize when it was stored in the dark. Therefore, this oxidation at the air–water interface cannot be a photooxygenation reaction or an oxidation similar to what was found for the electron-rich conjugated systems described above.^{15,16} A few other reports on oxidation reactions at the air–water interface have been published. Kamel et al.¹⁷ reported the oxidation of the hydroxyl group of cholesterol spread on a water subphase. This reaction could be prevented by dissolving ascorbic acid in the subphase, but the real oxidation reaction mechanism is unknown. Sagisaka et al.¹⁸ found that an amphiphilic aniline monolayer could be oligomerized without any oxidant such as persulfate, which usually is needed in this reaction. Our group reported a similar reaction¹⁹ in which a monolayer of hexadecyl-diaminobenzoate could be polymerized without a copper catalyst. No explanations have been reported for any of these unusual reactions.

Because the oxidation reaction of the monolayer was not reproducible (Figure 2), we supposed that environmental factors, such as the pH of the subphase and a variable composition of the unrestricted laboratory air, influenced the oxidation reaction. The pH of the subphase

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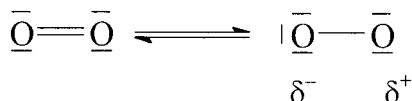


Figure 6. Chemical structure of polarized oxygen.

can alter a little because of variations in the dissolved amount of CO₂. To study the influence of the pH of the subphase, the pH was varied between 8.5 and 2.7, but no influence on the oxidation reaction was found. Blohm et al. observed that poly(thiophene vinylene) films are oxidized by ozone in unrestricted laboratory air.²⁰ To exclude a possible oxidation reaction with ozone the LB trough was placed under pure oxygen, but the oxidation reaction still took place. Moreover, the laboratory air was tested with Dräger tubes and no ozone was detected, which means that the ozone concentration was less than 0.05 ppm.

To elucidate whether free radicals are involved in the oxidation reaction mechanism either ascorbic acid or 3-carboxypropyl, both free radical scavengers, was dissolved in the subphase before the spreading of 32%-pcDMePPV, but the oxidation reaction was neither inhibited nor delayed.

Steinbach found an oxidative decomposition of oleic acid at the air–water interface.²¹ He assumed that oxygen at the air–water interface is polarized because of the anisotropy of the interface and that this would play an important role in this reaction. The tentative chemical structure of polarized oxygen is given in Figure 6.

Oxygen forms weakly bound complexes with double bonds.^{22,23} Therefore, Steinbach assumed that a complex between the double bond and polarized oxygen is formed at the interface and that this results in a reactive intermediate state, which might lower the activation energy. In this way the air–water interface works as a “catalyst”, lowering the activation threshold.

We assume that oxygen polarized at the air–water interface is also involved in the oxidation reaction described in this article. Additional circumstantial evi-

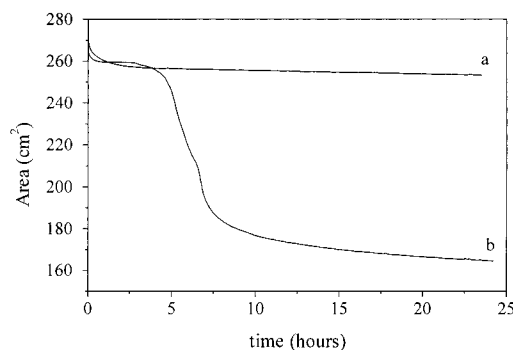


Figure 7. Stabilization curves of 32%pc-DMePPV with organic vapors in the atmosphere (a) and without organic vapors in the atmosphere (b).

dence for the involvement of polarized oxygen is that we accidentally discovered that the monolayer oxidation is delayed when organic vapors are present in the air above the monolayer. When 0.5 mL toluene was allowed to evaporate in the trough before spreading and the trough was sealed with tape, the stabilization curve shown in Figure 7a was obtained.

For comparison the stabilization curve of a monolayer without organic vapors is also shown in Figure 7b. The organic vapors are probably adsorbed at the air–water interface, and this might prevent the polarization of oxygen. The amount of organic vapors in a nonsealed trough stabilization experiment (Figure 2) varies; therefore, these experiments were not reproducible.

Conclusions

The double bonds of the PPV units of pc-DMePPV are oxidized at the air–water interface to aldehyde groups. This reaction also happens in the dark, so singlet oxygen is not involved in this reaction. Radical scavengers and the pH of the subphase have no influence on the rate of the oxidation reaction. It is likely that oxygen is polarized at the air–water interface and forms a weakly bound complex with the double bond. It is believed that this complex is a sort of reactive intermediate state. Adding organic vapors to the air above the monolayer prevents the oxidation reaction.

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